

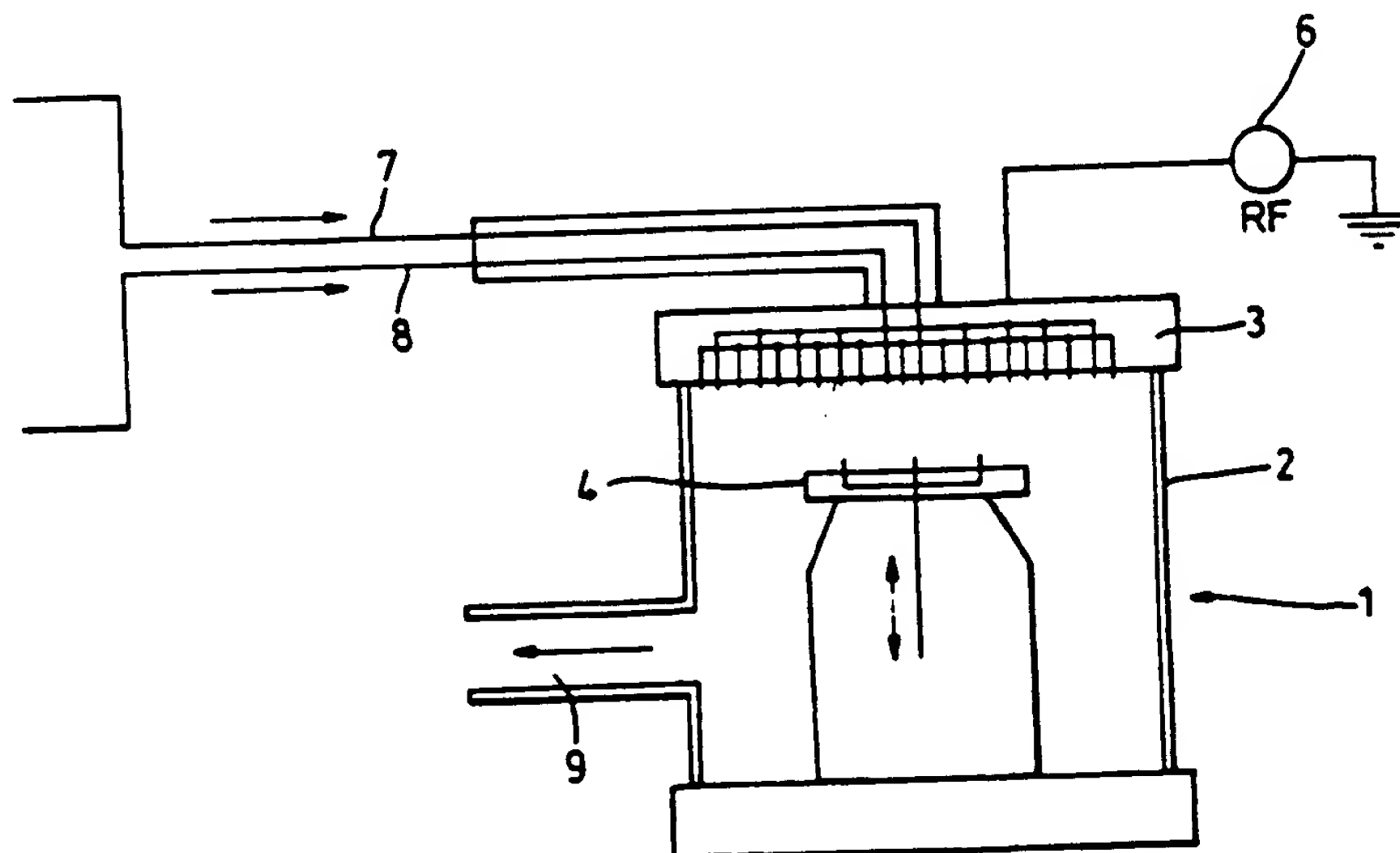
PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 : H01L 21/312, C23C 16/40	A1	(11) International Publication Number: WO 99/38202 (43) International Publication Date: 29 July 1999 (29.07.99)
(21) International Application Number: PCT/GB99/00191 (22) International Filing Date: 20 January 1999 (20.01.99) (30) Priority Data: 9801359.2 23 January 1998 (23.01.98) GB (71) Applicant (for all designated States except US): TRIKON EQUIPMENTS LIMITED [GB/GB]; Coed Rhedyn, Ringland Way, Newport, Gwent NP6 2TA (GB). (72) Inventors; and (75) Inventors/Applicants (for US only): CARTER, Steven [GB/GB]; 344 Warrington Road, Abram, Wigan WN2 5XA (GB). SHEARER, Christine, Janet [GB/GB]; 5 Stanley Street South, Bedminster, Bristol BS3 3PG (GB). (74) Agents: DUNLOP, Brian, Kenneth, Charles et al.; Wynne-Jones, Laine & James, Essex Place, 22 Rodney Road, Cheltenham, Gloucestershire GL50 1JJ (GB).	(81) Designated States: CN, DE, GB, JP, KR, US. Published With international search report.	

(54) Title: DEPOSITION OF A SILOXANE CONTAINING POLYMER



(57) Abstract

There is disclosed a method of treating a substrate, which method comprises positioning the substrate in a chamber (2), introducing into the chamber in the gaseous or vapour state a silicon-containing compound, a further compound containing peroxide bonding, and a substance which associates readily the compound containing peroxide bonding, the method further comprising the step of reacting the silicon-containing compound with the further compound and the soluble substance to provide on the substrate an insulating layer. Also disclosed is an apparatus for implementing the method.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakhstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

DEPOSITION OF A SILOXANE CONTAINING POLYMER

This invention relates to a method and apparatus for treating a substrate, such as a semiconductor wafer and, in particular, but not exclusively, to a method and apparatus for providing an increase in deposition rate of a high grade insulation layer. In addition, a low dielectric constant (known as low k) may also be provided by the method and apparatus of the present invention.

In the earlier Patent Application WO94/01885, the contents of which are incorporated herein by reference, a planarisation technique is described in which a liquid short-chain polymer is formed on a semiconductor wafer by reacting silane (SiH_4) or a higher silane with hydrogen peroxide (H_2O_2). In addition, the earlier co-pending Patent Application PCT/GB97/02240 discloses a method and apparatus for providing a low dielectric constant in a planarisation operation. The method disclosed utilises an organosilane compound and a compound containing peroxide bonding to provide a short-chain polymer as a deposition layer on a semiconductor substrate. It has been found that the reactants used in prior art processes provide very low deposition rates of the resulting polymer layer on the semiconductor substrate. For example, investigations into the reaction of phenylsilane and H_2O_2 yielded low deposition rates of the order of 600 Å/min.

The main purpose of the present invention is to put down a high grade insulation layer as rapidly as possible,

preferably without having a detrimental effect on the low dielectric constant of the insulator, and even improving the dielectric constant.

5 We have found that it is possible to increase significantly the deposition rates whilst maintaining other desirable properties, including a low dielectric constant, thereby improving the overall process of the deposition.

10 According to a first aspect of the present invention there is provided a method of treating a substrate, which method comprises positioning the substrate in a chamber, introducing into the chamber in the gaseous or vapour state a silicon-containing compound, a further compound containing peroxide bonding, and a substance which associates readily with the compound containing peroxide bonding, and reacting
15 the silicon-containing compound with the further compound and the associating substance to provide on the substrate an insulating layer.

20 Whilst the applicant is not to be restricted hereby, it is thought that the associating substance promotes the initiation between the compound containing peroxide bonding and the silicon-containing compound. Thus, the further compound, and the associating substance react with each other in the formation of the insulating layer.

25 The substance which associates readily with the compound containing peroxide bonding is preferably an oxidising agent, for example oxygen, ozone or tetraethoxysilane (TEOS). However, any material soluble in the compound containing peroxide bonding is appropriate, for

example carbon monoxide or carbon dioxide. The most preferred oxidising agent is oxygen.

The reaction which occurs is a chemical vapour deposition process and does not require an additional plasma, although such a plasma (for example a weakly ionised plasma) may, if required, be used within the process chamber. Thus, the reactants are preferably capable of reacting spontaneously. The reaction is thought to be a surface reaction.

The silicon-containing compound may be an organosilane, for example one of the general formula $C_xH_y-Si_nH_a$, or one of the general formula $(C_xH_y)_zSi_nH_a$, where x, y, z, n and a are any suitable values, for example integers.. The silicon containing compound is preferably of the general formula $R-SiH_3$. Preferably, R is a methyl, ethyl, phenyl, or vinyl group and it is particularly preferred that R is a phenyl or methyl group. Alternatively, the silicon-containing compound may be a silane (for example silane itself) or a higher silane. A further alternative is dimethylsilane. The silicon-containing compound is preferably not TEOS or other organometallic compound.

Any suitable combination of the components may be used but as will be understood by those skilled in the art certain combinations and pressures may not be appropriate as they are explosive in the chamber.

The compound containing peroxide bonding is preferably hydrogen peroxide.

In an alternative embodiment, the method may further

comprise the step of introducing an additional gas, for example nitrogen, into the chamber.

5 The associating substance can be introduced in any way. Thus, the associating substance may be pre-mixed with the compound containing peroxide bonding or the silicon-
10 containing compound prior to introduction into the chamber, although it has been observed that the deposition rate is particularly increased if the associating substance is pre-mixed with the compound containing peroxide bonding. Alternatively, the associating substance may be introduced
15 into the chamber as a separate component.

When R is a methyl group, eg. when methyl silane is the silicon-containing compound, the deposition rate is increased to about 1.1 $\mu\text{m}/\text{min}$. Thus when oxygen is used as
20 the associating substance the deposition rate was increased from about 8000 $\text{\AA}/\text{min}$ which was the rate in the case in which no oxygen was used. When R is a phenyl group the deposition rate is increased from about 600 $\text{\AA}/\text{min}$ to 2700 $\text{\AA}/\text{min}$. Furthermore, when oxygen is used as the associating
25 substance, the deposition rate when a silane or higher silane is used is increased from about 9000 $\text{\AA}/\text{min}$ to about 1.2 $\mu\text{m}/\text{min}$. In addition, it has been found that the addition of the associating substance, in particular oxygen, leads to a slight reduction in the dielectric constant of the film formed on the substrate, typically from 3.2 to 2.8.

A particularly preferred flow rate of the silicon-containing compound into the chamber is between 20 and 145 Sccm (3.4×10^{-2} to $0.24 \text{ Pa}\cdot\text{m}^3/\text{s}$), even more preferably about

45 Sccm ($7.6 \times 10^{-2} \text{Pa.m}^3/\text{s}$). The flow rate of the compound containing peroxide bonding into the chamber is preferably between 0.2 and 1.0 g/min and is even more preferably about 0.22 g/min. The flow rate of the associating substance into the chamber is preferably up to 50 Sccm ($8.4 \times 10^{-2} \text{Pa.m}^3/\text{s}$) and even more preferably is about 10 Sccm ($1.7 \times 10^{-2} \text{Pa.m}^3/\text{s}$). Above 20 Sccm spontaneous momentary pressure bursts are observed indicating vigorous reactions and rates above 50 Sccm may well therefore be unsafe in practice. Whilst any suitable pressure in the chamber, can be used, it has been found that appropriate pressures are below atmospheric pressure, for example in the range of 200 to 5000 mT, preferably about 1000 mT. When an further gas is used, its flow rate into the chamber is preferably between 50 and 1000 Sccm (8.4×10^{-2} to $1.7 \text{ Pa.m}^3/\text{s}$), even more preferably about 80 Sccm ($0.14 \text{ Pa.m}^3/\text{s}$). The units Sccm (Standard Cubic Centimetres per Minute) are at standard temperature and pressure.

The method may, if required, comprise the further step of removing water and/or OH from the layer formed from the short-chain polymer. Furthermore, the method may further comprise the step of forming or depositing an underlayer or a base layer prior to the deposition of the polymer layer. The method may further comprise the step of depositing or forming a capping layer on the surface of the formed layer and this layer is preferably applied in a PECVD process.

According to a second aspect of the present invention there is provided an apparatus for implementing the above

method which comprises means for introducing the components into the chamber and platen means for supporting the substrate. The apparatus may comprise a Chemical Vapour Deposition (CVD) or Plasma Enhanced Vapour Deposition process (PECVD) chamber.

Whilst the invention has been described above, it extends to any inventive combination of the features set out above or in the following description.

The invention will now be described, by way of example, with reference to the following example and the following drawing, and in which:

Figure 1 is a schematic view of an apparatus for performing the treatment method.

Referring to Figure 1, an apparatus for treating semiconductor wafers, or the like, is schematically illustrated at 1. The general construction of such an apparatus is well known in the art and therefore only the features which are relevant for the understanding of the invention are described. Thus, the apparatus 1 includes a chamber 2 having a duplex shower head 3 and a wafer support 4. The shower head 3 is connected to RF source 6 to form one electrode while the support 4 is earthed and forms another electrode. Alternatively, the RF source 6 could be connected to the support 4 and the shower head 3 earthed. The shower head 3 is connected by respective pipes 7 and 8 to a source of O_2 and H_2O_2 on the one hand and phenylsilane (C_6H_5Si) on the other hand.

In use, the apparatus is arranged to deposit a short

chain polymer on a semiconductor wafer or other substance
This may also provide planarisation either locally or
globally, or "gap filling". The polymer is formed by
introducing the components into the chamber, together with
5 a carrier gas, for example nitrogen, if required, and
reacting them within the chamber. The reaction may occur
spontaneously or may require initiation, for example from an
external energy source. The nitrogen may be needed to
improve the process due to the small flow rates of the other
10 components, and it may form part of the process. The flow
of the reactants is maintained at a desired level and they
are removed from the chamber via outlet 9. The resultant
polymer is deposited on the wafer. As regards the mechanism
involving oxygen, whilst the applicant is not to be
15 restricted hereby, it is believed that the O_2 is being
associated with the H_2O_2 , promoting the reaction between H_2O_2
and C_6H_5Si . The reaction may take place at the wafer
surface.

20

Example

Investigations into the reaction of phenylsilane
(C_6H_5Si) and H_2O_2 yielded very low deposition rates (of the
order of $600\text{\AA}/\text{min}$). In order to promote the reaction, a
25 small amount of additional oxidant - O_2 - was added to the
process which proved successful in increasing the deposition
rate to in excess of $2700\text{\AA}/\text{min}$.

The process used for the investigations was:-

		preferred process	range investigated
	C ₆ H ₈ Si (Sccm)	45	20 ---> 145
	H ₂ O ₂ (g/min)	0.22	0.2 ---> 1.0
5	N ₂ (Sccm)	80	50 ---> 1000
	O ₂ (Sccm)	10	0 ---> 50
	Pressure (mT)	1000	200 ---> 5000

10 As has already been mentioned it was found that, when the rate of O₂ flow is increased above 20 Sccm, an increasingly vigorous reaction occurred causing large fluctuations in chamber pressure.

15 Furthermore, the addition of O₂ has been found to increase the deposition rate of a process in which the silicon containing compound as a silane or higher silane from about 9000 Å/min to about 1.2 μm/min, and of a process in which MeSiH₃ is used from approximately 8000 Å/min to about 1.1 μm/min.

Claims

1. A method of treating a substrate, which method
5 comprises positioning the substrate in a chamber,
introducing into the chamber in the gaseous or vapour state
a silicon-containing compound, a further compound containing
peroxide bonding, and a substance which associates readily
10 with the compound containing peroxide bonding, and reacting
the silicon-containing compound with the further compound
and the associating substance to provide on the substrate a
an insulating layer.
2. A method according to Claim 1, wherein the associating
substance is an oxidising agent.
- 15 3. A method according to Claim 2, wherein the oxidising
agent is selected from oxygen, ozone, or tetraethoxysilane.
4. A method according to Claim 3, wherein the oxidising
agent is oxygen.
5. A method according to any preceding Claim, wherein
20 the silicon-containing compound is an organosilane of the
general formula $C_xH_y-Si_nH_m$ or $(C_xH_y)_nSi_nH_m$.
6. A method according to Claim 5, wherein the silicon-
containing compound is of the general formula $R-SiH_3$.
7. A method according to Claim 6 wherein R is a methyl,
25 ethyl, phenyl or vinyl group.
8. A method according to Claim 7, wherein R is a phenyl or
methyl group.
9. A method according to any one of Claims 1 to 4, wherein

the silicon-containing compound is a silane or a higher silane.

10. A method according to any preceding Claim, wherein the compound containing peroxide bonding is hydrogen peroxide.

5 11. A method according to any preceding Claim, further comprising introducing an additional gas into the chamber.

12. A method according to Claim 11, wherein the additional gas is nitrogen.

10 13. A method according to any preceding Claim, wherein the associating substance is premixed with the compound containing peroxide bonding or the silicon-containing compound prior to introduction into the chamber.

14. A method according to any one of Claims 1 to 12, wherein the associating substance is introduced into the chamber as a separate component.

15 15. A method according to Claim 8, wherein, when R is a methyl group, the deposition rate is increased to about 1.1 $\mu\text{m}/\text{min}$.

20 16. A method according to Claim 8, wherein, when R is a Phenyl group, the deposition rate is increased to about 2700 $\text{\AA}/\text{min}$.

17. A method according to Claim 9, wherein the deposition rate is increased to about 1.2 $\mu\text{m}/\text{min}$.

25 18. A method according to any preceding Claim, wherein the flow rate of the silicon-containing compound into the chamber is between 20 and 145 Sccm.

19. A method according to any preceding Claim, wherein the flow rate of the compound containing peroxide bonding into

the chamber is between 0.2 and 1.0 g/min.

20. A method according to any preceding Claim, wherein the flow rate of the associating substance into the chamber is up to 50 Sccm.

5 21. A method according to Claim 11 or 12, wherein the flow rate of the additional gas into the chamber is between 50 and 1000 Sccm.

22. A method according to any preceding claim, wherein the pressure in the chamber is below atmospheric pressure.

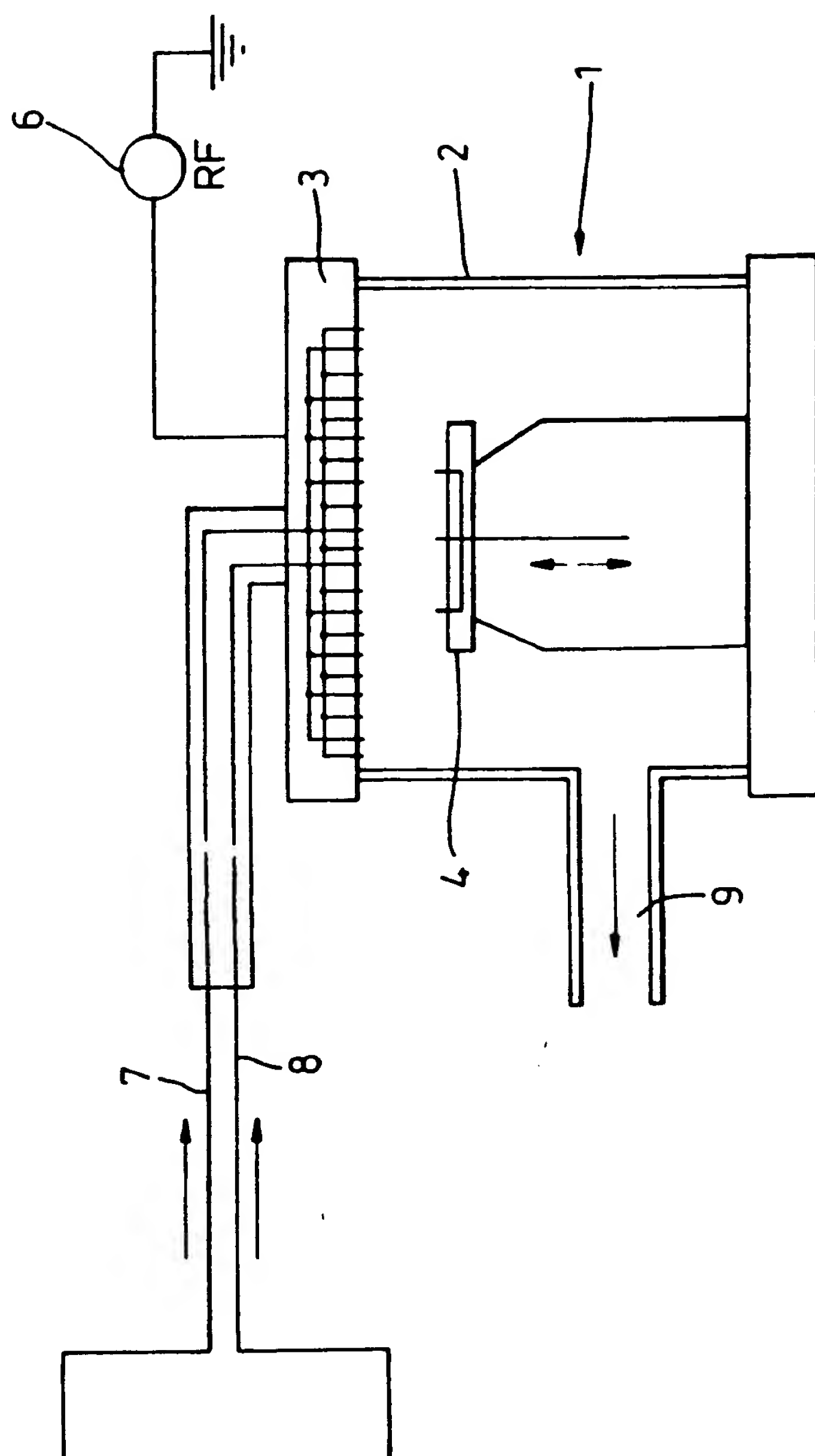
10 23. A method substantially as hereinbefore described, with reference to, and as illustrated in, the accompanying example and drawing.

24. An apparatus for implementing the method of any preceding Claim, including means for introducing the components into the chamber and platen means for supporting the semiconductor substrate.

15 25. An apparatus according to Claim 24, comprising a CVD and/or a PECVD chamber.

20 26. An apparatus substantially as hereinbefore described with reference to, and as illustrated in, the accompanying drawing.

1/1

*Fig. 1*

INTERNATIONAL SEARCH REPORT

International Application No
PCT/GB 99/00191

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 H01L21/312 C23C16/40

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 H01L C23C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 440 154 A (APPLIED MATERIALS INC) 7 August 1991 see column 4, line 30 - line 39 see column 5, line 3 - line 8 ---	1-4, 10-13, 18,22-26
X	PATENT ABSTRACTS OF JAPAN vol. 096, no. 012, 26 December 1996 & JP 08 213378 A (HITACHI ELECTRON ENG CO LTD), 20 August 1996 see abstract ---	1-3, 10-12, 22-26
X	EP 0 742 290 A (AIR PROD & CHEM) 13 November 1996 see abstract --- -/-	1-3

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- "&" document member of the same patent family

Date of the actual completion of the international search

27 April 1999

Date of mailing of the international search report

06/05/1999

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Königstein, C

INTERNATIONAL SEARCH REPORT

In International Application No
PCT/GB 99/00191

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 94 01885 A (DOBSON CHRISTOPHER DAVID) 20 January 1994 see figure 1	1,24,25
A	--- DOBSON C D ET AL: "ADVANCED SiO2 PLANARIZATION USING SILANE AND H2O2" SEMICONDUCTOR INTERNATIONAL, vol. 17, no. 14, December 1994, page 85/86, 88 XP000671223 see the whole document	1
P,X	--- PATENT ABSTRACTS OF JAPAN vol. 098, no. 013, 30 November 1998 & JP 10 209148 A (SONY CORP), 7 August 1998 see abstract -----	1

INTERNATIONAL SEARCH REPORT

Information on patent family members

In: International Application No

PCT/GB 99/00191

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 0440154	A	07-08-1991	US 5314845 A	24-05-1994
			DE 69118727 D	23-05-1996
			DE 69118727 T	12-12-1996
			ES 2088783 T	16-09-1996
			JP 4213829 A	04-08-1992

EP 0742290	A	13-11-1996	US 5637351 A	10-06-1997
			JP 9027487 A	28-01-1997

WO 9401885	A	20-01-1994	AU 4506993 A	31-01-1994
			CA 2137928 A	20-01-1994
			CN 1089757 A	20-07-1994
			EP 0731982 A	18-09-1996
			JP 9502301 T	04-03-1997
			US 5874367 A	23-02-1999
